Activation of end of life tyres pyrolytic char for enhancing viability of pyrolysis – Critical review, analysis and recommendations for a hybrid dual system

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ABSTRACT

Taking under consideration the environmental boundaries but also the minimization of operating cost, End of Life Tyres (ELTs) depolymerization technology, via pyrolysis, can be characterized viable, under the condition of the effective valorization of every produced stream. This study aims to investigate which factors determine the path to activated carbon production from tyre-derived char, assuring that the received product will be of accepted quality, thus setting it as a commercially competitive product. To obtain current information on char activation, a comprehensive literature review was undertaken. An assessment based on process parameters, economic aspects and proposed uses of the produced activated carbons, was also presented. The proper selection of activation conditions (time, temperature, activating agent) results to a carbon adsorbent with prescript physical and chemical properties, suitable for specific applications. Towards energy self-sufficiency of the whole plant, a number of recommendations were made for the dual pyrolysis-activation scheme. Eventually, this would be an extra asset for the proposed valorization route of ELTs, via pyrolysis process.

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1. Introduction

Generally, almost every ground transportation need is met through vehicles of any kind. As a result, a huge amount of used tyres is generated every year globally. Recent statistical data show a 5% increase of global tyres production in 2011, compared to 2010, reaching 14.68 million tons [1–3]. Asia and Oceania account for almost 60% of the global production (Fig. 1). On the other hand, Japan disposes one million tons of tyres every year while China, generated 5.2 million tons in year 2010, becoming one of the countries with largest production of used tyres [4,5].

The disposal of End of Life Tyres (ELTs) is a serious environmental issue. Although they constitute a problem, at the same time they provide valid opportunities for resources conservation, since they represent waste materials with great potentials as for recovering of valuable materials and fuels [6]. Tyres are a co-polymer of long-chain polymers including isoprene, styrene and butadiene that are cross-linked with the addition of sulphur (vulcanization). Small amounts of inorganic constituents are also used during their manufacturing process.
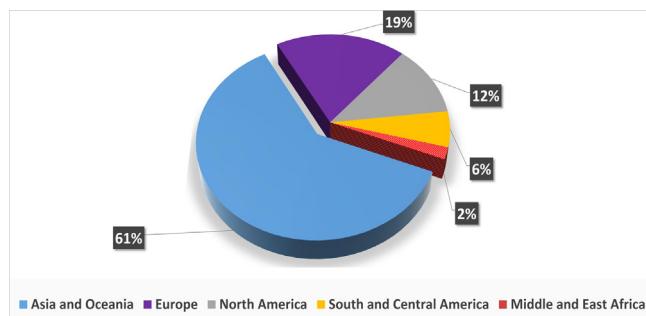
Several techniques and methods regarding ELTs management, including retreating and reclamation, were applied [5,7]. Recycling as a management route, despite its broad acceptance still includes high cost processes, also resulting to end products with questionable characteristics [8]. On the other hand, the most common thermal application of used tyres is in fact, their use as a supplementary fuel in cement kilns (co-combustion) [9,10]. Alternatively, pyrolysis and less frequently gasification are proposed. However, the latter mostly refer to experimental and pilot scale processes.

Pyrolysis attracted much attention due to the characteristics of the expected products. During pyrolysis, heat is supplied at an inert atmosphere to ELTs that decompose via a large number of thermal cracking reactions to a series of gas, liquid and solid products. Research work on ELTs pyrolysis began two decades ago and continues up to date, through the implementation of novel methods and techniques, while focusing mainly on the effect of operating conditions on product yields and on products′ qualitative characteristics [11,12]. Few pilot and industrial scale plants were constructed and operated, adopting the prior experience on ELTs pyrolysis [13–24]. Based on the above mentioned developments, used tyres pyrolysis was introduced in industry as a mature technology offering a proven alternative to the disposal of this waste material. Specialized equipment suppliers are scattered worldwide, providing turn-key solutions and expertise, especially for ELTs pyrolysis. Despite these developments and the experience gained from operating plants, some intrinsic problems characterize ELTs pyrolysis as less attractive than expected; thus, not promoting its advantageous characteristics over incineration process [25]. The major obstacle to be overcome, is related with the disposal of process products and especially, of pyrolysis oil and residual carbon black; pyrolysis gas can be consumed in-plant, to fulfil the energy needs of the pyrolysis kiln.

The implementation of pyrolysis, as an alternative waste management process should aim to sustainability, through the

Fig. 1. World tyre global production (2011).
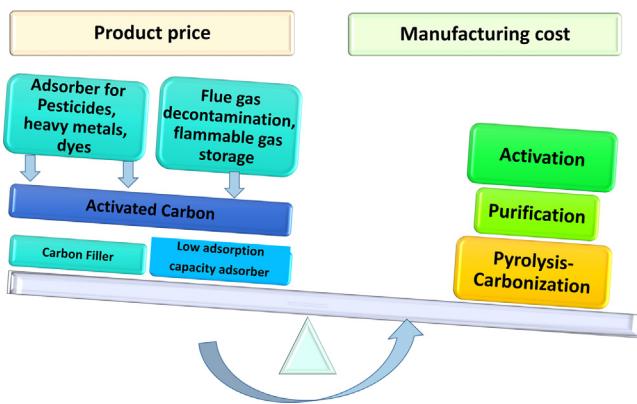
Fig. 2. Depolymerization economics [10].

valorization of every product received. The incapability of addressing the above, can characterize an investment/endeavour as non-attractive. Furthermore, it is highly important to spot adequate product uses and niche markets that can provide economic benefits, while assisting to the minimization of pyrolysis process cost. The thermochemical valorization of both pyrolytic gas and pyrolytic oil, along with the upgrading of the surface and structural characteristics of pyrolytic char, can contribute effectively to increase the viability of the ELTs depolymerization plant.

In this context, the technical and economic features of both processes, pyrolysis and activation, for the efficient production of an eco-friendly and cost effective adsorptive material from ELTs, are analysed. This effort aims to reverse the negative effect of processes′ cost, as depicted in Fig. 2. The study is part of an EU LIFE+ project [26] whose objective is to contribute to the implementation, updating and development of EU environmental policy with European added value.

2. Pyrolysis products

ELTs pyrolysis results to gaseous, liquid (pyro-oil) and solid (char) products. Product yields depend mainly on pyrolysis temperature, pressure and residence time. Pyrolysis gas yield increases with temperature; the maximum value recorded, exceeds 30 wt%. Pyrolysis oil yield marks a maximum value of about 50 wt%; a further increase of pyrolysis temperature results to decreased yields [15]. Char yield, based on literature findings, varies between 33–49 wt%. Those data were obtained at temperatures ranging between 400 °C and 800 °C [27–29]. Regarding pressure impact on ELTs pyrolysis, reduced pressure or vacuum (0.25 atm) can result to lower energy requirements for the process, higher liquid yield, and better quality of the received solid [28,30]. Residence time impact on ELTs pyrolysis is directly connected to ELTs particle size. ELTs particles of bigger dimensions require longer residence times, resulting evidently to decreased efficiencies of the pyrolysis unit [27–29]. The obtained pyrolysis products have been extensively tested, either they originated from laboratory or pilot scale units [11,12,31,32]. Data from small scale industrial units are also reported [15].

Catalytic pyrolysis of waste tyres, generally aims to maximize liquid yield. However, the addition of catalysts does not always assure improved liquid yield and an additive is required (lubricant base oil). In this case, increased production of liquids as well as, increased production of limonene ($\sim$13.6 wt%) are anticipated. [33]. Additionally, more high-added value chemicals, including limonene, xylene, benzene can be produced [34,35]. This could promote the alternative use of pyrolysis oil to improve plant

economics, through the extraction and ultimately, sale of valuable chemicals.

2.1. ELTs pyrolysis gas

Pyrolysis gas as a result from the thermal decomposition of the raw material, is composed of carbon oxides, hydrocarbons (methane, C_2-, C_3-, C_4-), hydrogen (H_2) and hydrogen sulphide (H_2S) [27–29,36]. As temperature rises, the heavier hydrocarbons are cracked, giving rise to lighter ones (methane and ethane) as well as to hydrogen, increasing simultaneously the volume of the produced gas. The calculated lower heating value of the produced gas exhibits high values, ranging between 30 and 45 MJ kg^{-1}, thus characterizing it as an efficient means to provide energy for pyrolysis process [31,32].

However, in order to maximize the advantages of pyrolysis gas valorization through electricity generation via customized burners/boilers, a purification process is proposed. This targets mainly to eliminate the negative effects (undesirable SO_2 emissions) stemming from the combustion of the contained hydrogen sulphide on the received product. Purification of the gaseous stream originated from ELTs pyrolysis gas combustion can be performed in several appliances including wet scrubbing, wet sulphuric acid process and spray-dry scrubbing and SNOX process [37,38]. In another study for cost reduction reasons, part of the purified pyrolysis gas was used as the carrier gas, while the rest of the gas and the pyrolysis char were used as the heat source for the process [38,39].

2.2. ELTs pyrolysis oil

The complex composition of ELTs pyrolysis oil is attributed to the various rubbers (natural rubber (NR), styrene–butadiene rubber (SBR) and butadiene rubber (BR)), Carbon Black and additives (vulcanization agents and accelerators) used during their manufacturing process [40,41]. More specifically aromatics, non-aromatics, nitrogen, oxygen and sulphur compounds consist the complex mixture of ELTs pyrolytic oil [42]. The results from elemental analyses from various experimental apparatus exhibited a C/H ratio exceeding value 8 (higher molecular weight compounds/multiple ring structures), as well as high calorific values ranging from 27.8 up to 44.8 MJ kg^{-1}, depending on the operational parameters applied. Variations on pyrolysis temperature affected primarily the composition on aromatics and aliphatics (increased pyrolysis temperature favours aromatic formation reactions, including Diels–Alder reaction) and in a lesser extent, C/H ratio and calorific value [42].

Pyrolysis oil (pyro-oil) has attracted considerable interest as a fuel; in fact, it is proposed to be used in boilers and diesel engines. Boiler fuel seems to be the most convenient application of pyro-oil. Many works conclude that it is comparable to diesel-oil, since it is a fuel of high energy content while its sulphur content does not exceed 1.4 wt%; therefore, it can be used as a substitute, totally or partly, of the diesel-oil in industrial applications [27–29,43]. The heating value of tyre pyrolysis oil is similar to that of fossil fuels, whereas biomass-based pyrolysis oil exhibits lower LHV values, due to the increased number of oxygenated compounds and increased water percentage [27,44]. However, this conclusion is questioned by some authors [45]. Moreover, research work was carried-out to determine if any valuable components, of high commercial value, could be extracted; limonene, xylene, benzene are the most frequently encountered substances of this category [34]. Limonene production is mostly attributed to the decomposition mechanism of NR, can be used in the formulation of industrial solvents, resins and adhesives and as a dispersing agent for pigments; however, its yield decreases with increasing

final pyrolysis temperature due to its instability at higher temperatures [40].

Sulphur content is the major concern in pyro-oil. To overcome this difficulty, process temperature can be controlled to obtain a low-sulphur content oil. It is generally concluded that sulphur concentration in oil, increases with pyrolysis temperature. In order to lessen the effect of this undesired characteristic, oil desulphurization methods along with high vapour filtration and liquid filtration have been proposed [44,46]. However, specialized equipment constructors offer combustion equipment (burners, boilers) customized for pyrolysis oils, further strengthening the perception for produced oil usability, as a fuel [47]. Alternatively, synthesis gas production is also achievable, through gasification of pyrolysis oil. Steam gasification of pyrolysis oil using calcined dolomite, results to a high LHV gas [48].

Pyrolysis oil has several environmental advantages over fossil fuels, since it is CO_2/GHG neutral. No additional SO_x/NO_x emissions are anticipated, due to low sulphur percentage in raw material. However, the lack of established or approved standards for pyrolysis's oil quality and properties, prohibits the general use of pyro-oil as fuel. This is certainly an important drawback able to decelerate the development of ELTs pyrolysis plants to a larger scale. Moreover, certain undesired characteristics of the produced oil are also noticed, including the presence of alkali metals and char particles in the produced oil, low PH values, high viscosity, high water content, incompatibility with some polymers, high temperature sensitivity and inhomogeneity. As a result, the in-plant consumption of the produced pyrolytic oil in order to fulfil internal energy requirements remains the only practical option.

Alternatively and with the perspective of broadening the area of probable users, the use of ELTs pyrolytic oil in mixtures was investigated thoroughly during the past years, mostly in common diesel engines [17,49–51]. A published study proved that engine tests performed in diesel engines using fuel mixtures (20 vol% of ELTs pyrolysis oil with diesel) did not require any engine modifications [22]. Moreover, despite the fact that a fuel mixture with 5 vol%. ELTs pyrolysis oil is responsible for a slightly increased engine load of the automotive diesel engine tested and a reduced catalytic activity, ELTs pyrolysis oil can become a novel source of alternative fuels; desulfuration and distillation of the produced ELTs pyrolysis oil, should be considered mandatory though [17,28] Further issues to be addressed, are the increased carbon monoxide, hydrocarbon and nitrogen oxide emissions, as well as smoke opacity [49,52]. Towards the improvement of ELTs pyrolysis oil characteristics, the co-pyrolysis of biomass and ELTs, due to the synergetic effect developed between two feedstocks, resulted in better characteristics of the received oil (single phase fuel, increased LHV, reduced water content) [53].

2.3. ELTs pyrolysis char

Char yield from ELTs pyrolysis strongly depends on their composition and operation parameters and varies between 35 and 40 wt%. ELTs pyrolysis char is a mesoporous material with a calorific value between 28–32 MJ kg^{-1}. In general, it is a solid material of high carbon percentage (> 80 wt%), low hydrogen, nitrogen and sulphur content(< 2 wt%, < 2 wt% and < 3 wt%, respectively). Sulphur content in ELTs pyrolysis char is calculated to be about 50% of the initial sulphur present in tyres (vulcanization), [54,55]. The moisture content is low (< 5 wt%) due to the operational conditions. The same is valid for volatiles content (< 5 wt%). Results from published works either of experimental or industrial scale, report three independent routes for char valorization. More specifically, char can either be: (i) a fuel for combustion, (ii) gasified producing syngas or (iii) upgraded to high added value carbonaceous products (carbon black or activated carbons)
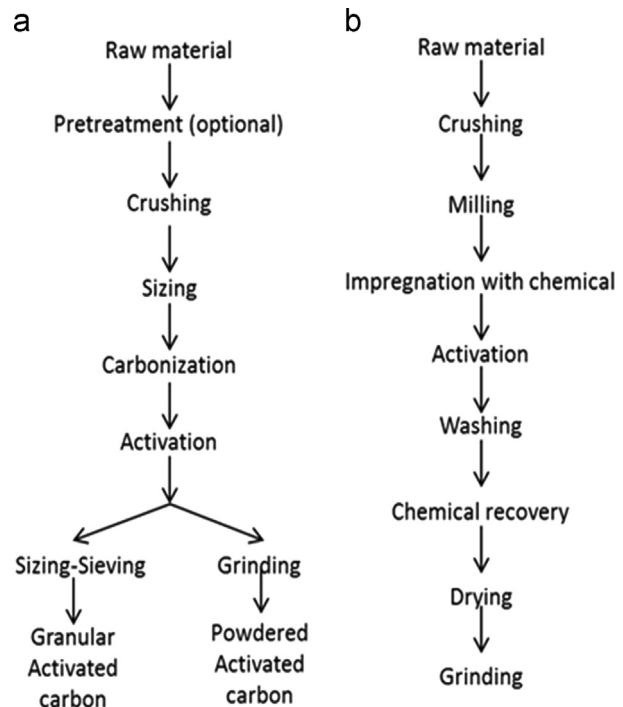
Fig. 3. Flow sheet of activated carbon production from ELTs (a) by physical activation and (b) by chemical activation.

[56–62]. Additionally, an emerging application of ELTs char, due to its structural characteristics is their use in sulphur-doped porous carbons manufacturing, as a result of sulphur impregnation in high temperatures ($T > 800$ °C) [63,64]. The received products may be utilized in a wide range of applications including catalyst support (sulphur species are often used as the capping agents for metal particles), sorption operations, as well as in the areas of energy conversion and storage applications [65–67].

Ash content (< 15 wt%), on the other hand, is attributed to increased minerals presence (mainly Zn) during tyres manufacturing. The variety of commercial carbon blacks used in tyre manufacturing also influences the characteristics of the char, ultimately resulting in a heterogenous solid material of high ash content and low adsorption capacity ($S_{BET} < 100$ m^2 g^{-1}) [27–29]. The BET surface area was calculated by the Brunauer, Emmett, and Teller (BET) method using the adsorption isotherms. Ash is preferred to be removed prior to any further valorization operation (activation); in a different case, ash content will grow dramatically, due to the high burn-off carbon losses. Burn-off is defined as the weight difference between ELTs char and activated carbon divided by the weight of ELTs char, with both weights on a dry basis [68]. A typical carbon black used in tyre manufacturing must have an ash content below 0.5 wt% [69]. Additional desired characteristics include also a well-developed homogenous porous structure and attractive structural characteristics.

3. Activation

Activated carbon production is a combined effect of two different processes: (a) carbonization of the raw material, where the carbon content is enriched and an initial porosity is created and (b) the consequent process, activation of the solid product, where the pore structure enhancement takes place [70,71].

Carbonization of the raw material: This process comprises of a series of pyrolysis reactions by which "volatile" matter and most of the inorganic materials (H_2, O_2, S, N) are released from the carbon
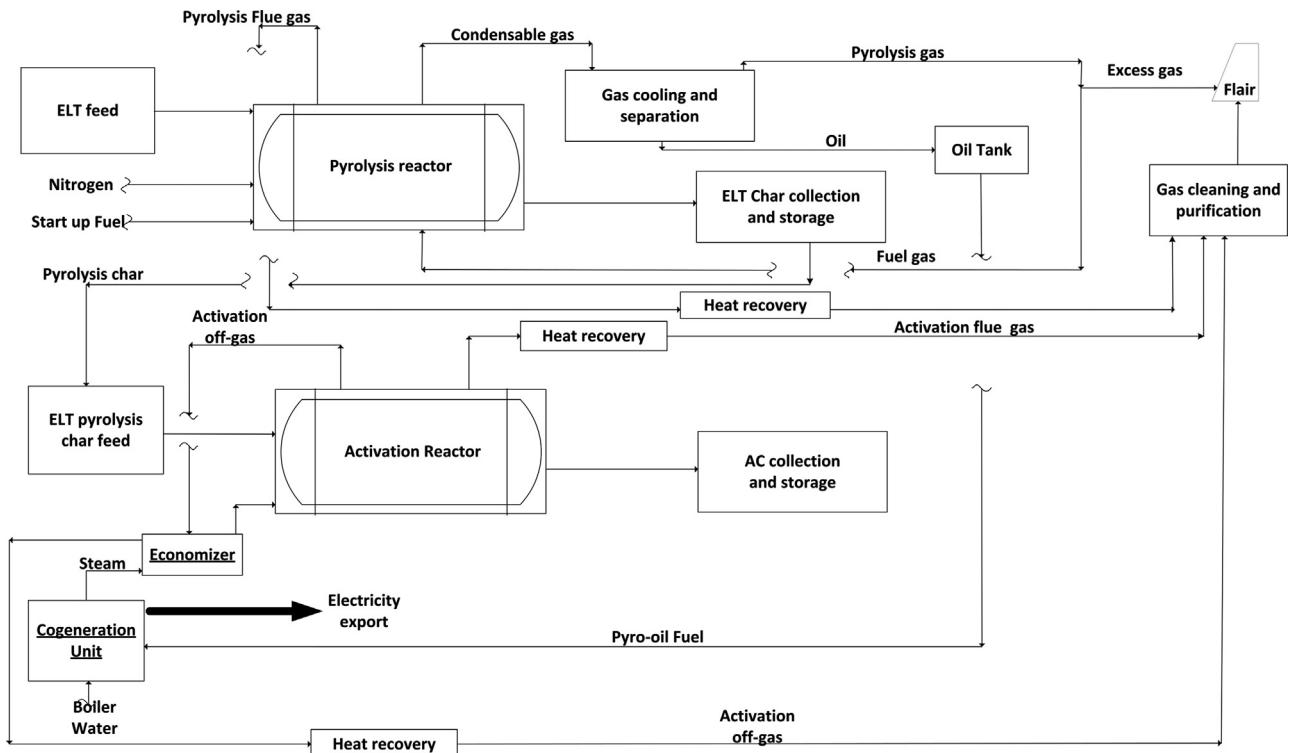
**Fig. 4.** Block diagram of activated carbon production from ELTs.

matrix by thermal decomposition, resulting to gaseous and solid products. The solid product (pyrolysis char) exhibits a structure, dominated by graphite-like crystallites. The free space between them, during carbonization, can be filled with disorganized carbon, originated from the deposition of tarry substances that takes place in parallel to the decomposition reactions. Therefore, chars exhibit low porosity values. A drastic porosity increase can be achieved through activation process.

Activation of the char: The freed space between crystallites constitutes the porosity. Removal of disorganized carbon is, most commonly, obtained through partial gasification – called "physical" activation of carbon material with "activating agents" such as steam, CO_2, air or a combination of them. The basic activation reactions are as follows:

$$C + H_2O \rightarrow CO + H_2 \tag{1}$$

$$C + CO_2 \rightarrow 2CO \tag{2}$$

$$C + O_2 \rightarrow CO_2 \tag{3}$$
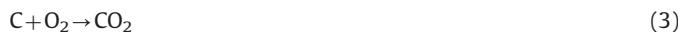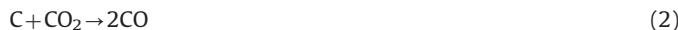
The first two reactions are used in practice. The larger dimensions of CO_2 molecules, compared to those of H_2O, result in a slower CO_2 pore diffusion, as well as to a lower accessibility to micropores. Both activation processes are endothermic, creating the need for heat supply to the gasification/activation reactor. Generally, CO_2 activation occurs preferably at higher temperatures and reaction times ($T > 900\ °C$ for several hours). On the contrary, steam gasification requires lower temperatures, ($T > 800\ °C$), and even shorter residence times (2–3 h) depending on raw material used [57].

Air or O_2 is not used as an activating agent due to the increase of the reaction rate. Carbon is consumed at the external surface area without creating porosity. During char activation, the disorganized carbon is removed (by the gasification reactions) at first. This corresponds to a 10–20% of weight-loss (burn off). Continuously, additional carbon atoms from primary crystallites are

consumed by the activating agent, creating new pores or/and enlarging some of the existing ones. As gasification reactions progress, the burn-off levels of carbon material are increased, developing further the porosity. Porosity development depends on carbon burn-off, the mechanism of carbon removal and the relative rate of reaction in each direction, parallel or vertical to the level of graphitic layers.

Alternatively, carbonization and activation can be carried out with the addition and/or impregnation of a substance, which restricts the formation of tarry products (chemical activation). The most common activating agents are $ZnCl_2$, H_3PO_4, and KOH. The resulting carbon is obtained in a single stage mechanism resulting also in a well-developed pore structure.

3.1. Physical activation

Physical activation involves two stages of treatment, carbonization and activation; the process is presented in a simplified flow sheet (Fig. 3a). Initially, the raw material undergoes a size-reduction process and then is fed to the pyrolysis/carbonization reactor for its de-volatilization. Subsequently, the received product is activated in a second reactor with steam (or CO_2); the produced activated carbon is cooled and further treated, according to the physical form requested, either granular (Granular Activated Carbon – GAC) or powdered (Powdered Activated Carbon – PAC).

If a pelletized activated carbon is proposed to be produced, modifications (additional mechanical equipment) on the process are required. More specifically, the raw material should be crushed, milled, extruded in the desired form, dried and then carbonized and activated normally [72]. Detailed process flow sheets for activated carbon are scarce in international literature. Only general, simplified flow plans can be found.

In this study, it is suggested that a two-stage process scheme (hybrid dual process unit), should be comprised of the following (Figs. 3a, 4):

Raw material storage and feed in system: This section can include a storage silo, and a system of screw feeders or belt conveyors, with air-lock valves to avoid air intrusion to the pyrolysis reactor.

Pyrolysis and activation kilns: in most of the cases, rotary kilns are used as pyrolysis and activation reactors. Rotary kilns are selected not only because of the stability of reaction conditions but also because of the advantages stemming from the mechanical treatment of the ELTs during pyrolysis [73].

Kilns usually, are indirectly heated (gas burners).

Char transportation system from pyrolysis to activation chambers is required. It should be able to operate at high temperatures and air-tight conditions.

A pyrolysis gas cooling–cleaning system: gas should be recycled to kiln burner for energy conservation.

A pyrolysis liquid cooling and storage system, regarding that operating parameters will result in liquid products.

A steam production unit and a supply circuit to the activation reactor (in the case of steam activation).

Cooling–screening–storage and packaging system of the produced activated carbon.

The operation of the proposed dual system can be continuous or batch. For a batch operation, one heating chamber can be used intermittently for carbonization and activation.

3.2. Chemical activation

Every chemical agent used, is in fact a dehydrating agent that influences pyrolytic decomposition and inhibits tar formation, thus enhancing the carbon yield. Because of the dehydrogenation properties of the agents used, the formation of a rigid matrix is promoted by cross-linking reactions, making them also less prone to any further volatile loss and volume contraction upon carbonization [74,75]. At the end of the process, the used chemical agent has to be removed by washing; in most cases, the activated carbon is at this stage eligible for use. During chemical activation, the raw material is impregnated with the activating agent, mostly KOH and H_3PO_4; $ZnCl_2$ is not used in current practice, due to environmental concerns regarding Zn emissions to environment. The process according to Fig. 3b, must include a H_3PO_4 solution preparation step, a raw material-solution contact device and a H_3PO_4 recovery and recycle system.

The mechanism of pore formation during chemical activation is different than that of physical. It relies on the fact that the agent penetrates the carbon structure, acting as a template for porosity development, although other phenomena are involved. By the time the product is washed-out from the incorporated chemical in the carbon structure, the interstices created, constitute the new porosity of the samples. Therefore, the carbon yield tends to be greater than in physical activation, since excessive carbon burn-off is not required for pore creation. Activation reaction strongly depends on the concentration of chemical agent, degree of mixing, temperature and activation duration (for the three most common activating agents $ZnCl_2$ is preferred at temperatures $< 500\,°C$, $H_3PO_4 < 450\,°C$ and KOH $> 700\,°C$) [70].

This process is an one step process, since carbonization and activation are completed in the same reactor [72].

3.3. Type of reactors

Activated carbon production relies on the thermal treatment of the carbonaceous material either in two stages (for physical activation), or in one stage for chemical activation. During physical activation, superheated steam and/or carbon dioxide are used as activating agents. In the chemical activation, the raw material is mixed with the chemical agent (KOH, H_3PO_4, $ZnCl_2$) and is

consequently heated to the prescribed temperature. As activating reactors employ high temperatures, the most common types include the rotary kilns, the multiple hearths, and the fluidized beds.

Although all stages of activated carbon manufacturing are important, since they can determine the properties of the product, the heating conditions require special attention and tight control, since furnace can be categorized as an expensive piece of equipment, mostly custom-designed for each plant. In this regard, it can be concluded that, for a certain type of activated carbon, the adequate type of furnace, is required.

3.3.1. Multiple hearth furnaces

Multiple hearth furnaces were originally developed for mineral ore roasting nearly a century ago and are currently used in carbonization and regeneration of activated carbon, as well as in other similar processes like pyrolysis/incineration of solid fuels. The basic form of a multiple hearth furnace (MHF) contains a vertically oriented steel cylinder. A MHF consists of a series of circular hearths, placed one above the other and a vertical rotating shaft with rabble blades through the centre of the furnace. Material is fed to the top hearth and rambles across to pass through drop holes to the lower hearth. It passes in this way, over and across each hearth, towards the bottom of the reactor, where the product is finally discharged through one or more ports. Meanwhile, the heated gases flow counter-currently to heat the charge to reaction temperature, assuring the continuity of the reaction. Despite the fact that multiple hearth furnace is an option for thermal processes of only few solid materials (sewage sludge incineration and tyre char activation), it permits many structural variations to accommodate special operations. Temperature, residence time, atmosphere, supplied energy and produced gases can be totally controlled and managed, assuring at the same time, product's uniformity by the gentle rumbling, turning and mixing of the material. With MHF, an improved gas-solid contact is achieved, while the temperature difference between the top and the bottom of the material is minimized [76,77].

3.3.2. Fluidized bed reactors

A fluidized bed reactor's design is based on the fluidization of a bed of grainy porous material, achieving a uniform temperature distribution and better solid–gas contact and heat transfer rates. The bed is mixed and agitated, keeping small inert particles and air in a fluid-like state; finally, the raw material, gas and sand are fully circulated through the reactor. Air, CO_2, steam or mixtures of them are injected into the reactor from the bottom through a gas distributor. FBRs are also equipped with cyclone separators in the top section, for the removal of the particulates from the product stream [78].

Based on literature findings, fluidized-bed gasification of ELTs targets mostly to gas production (LHV between 6 and 15 MJ NM^{-3}) [79,80]. However, if targeted to activated carbon production, the received products exhibit BET surface area values, up to 732 m^2 g^{-1} [81]. In industrial scale, some companies have already adopted fluidized bed furnaces for the activated carbon production [82,83].

3.3.3. Rotary kiln reactor

A rotary kiln is a cylindrical vessel, inclined slightly to the horizontal, which rotates slowly about its axis. The material to be processed is fed into the upper end of the cylinder. As the kiln rotates, the raw material gradually moves towards the lower end. A rotary kiln is provided internally with appropriate lifters, to ensure the desired homogeneity of the heat treatment.

There are two types of rotary kilns regarding the heat supply mode: the direct and the indirect type. In the first case, heating is accomplished by supplying fuel directly inside the furnace; the raw material to be treated is in contact with flue gases. Most companies use this type of kilns to produce activated carbons, of a larger particle size. Direct fired kilns are lined with refractory materials for several reasons; the primary purposes are, to insulate and protect the outer shell in high temperature applications from thermal damage, as well as to preserve energy. Kilns may also be equipped with dams to increase the material dwell time, or with lifters and tumblers, to aid the materials to flow axially and in some cases, to improve particle mixing which can be achieved through surface renewal. These furnaces are of larger dimensions and for this reason, heating is always direct and consequently, several burners and gas supply lines are distributed along and around the kiln's casing, to control gas composition and temperature across the kiln.

In indirectly fired rotary kilns, heat is supplied externally; this is the preferred type for small plants directed to activated carbon production. They are usually designed for applications, where direct contact between the material and the energy medium (providing the heat source) is undesirable. In this case, the heat source is placed externally, next to the kiln. Any internally flowing gas, is used for purging any volatile or gas that arises from the bed, as a result of chemical/physical (activation) reactions.

The present study recommends a rotary kiln for ELTs char activation. A unique feature of indirect-fired rotary kilns is that they can provide multiple and compartmentalized temperature control zones, which can be electrically heated or gas fired individually. Therefore, they provide the capability of achieving high temperatures. In rotary kilns, the temperature varies along the kiln axis in a complex mode and depends in a series of process parameters like steam flow rate, as well as carbon feed and carbon production rate. The solid residence time in rotary kilns is much longer than in other types of furnaces and can be controlled by using variable speed motors for the rotation of the furnace. During physical activation with steam, the agent should be supplied as superheated steam, to avoid condensation inside the kiln.

3.4. Conditions affecting activated carbon quality

Activated carbons are mostly used in gas and liquid phase applications. The suitability of an activated carbon for a specific application is determined by two fundamental parameters: (a) maximum adsorption capacity and (b) rate of adsorption, as calculated from the experimental adsorption isotherm and kinetic data.

These two factors are inherently connected with the pore structure and particle size of the product. In general, an activated carbon comprises of either micropores (less than 20 Å) and/or mesopores (20–500 Å) [84,85]. The pore size distribution in the sample varies, since it is strongly dependent on activation operating conditions. Adsorption capacity is related to the carbon conversion degree (expressed in weight percentage (wt%), or conversion). Adsorption capacity also depends on adsorbate's molecular dimensions. In this regard, the degree of accessibility of the adsorbate in the internal pore surface area, is the most crucial parameter. More specifically, the adsorption of large organic molecules requires high surface areas, in the mesopore range of sizes, since the entrance in micropores is obviously size-excluded. High values of micropore volumes lead always in high surface areas, with minor dependence on activating conditions. Furthermore, micropores are responsible for phenomena such as molecular sieving and irreversible adsorption. The last occurs in high adsorption energy sites that are responsible for increased carbon removal during activation [86].

The kinetics of adsorption rate depends also on pore size, size of adsorbent molecules and on the state of solvent used. Generally, in gas phase adsorption, diffusion does not limit the process and adsorption is predominant. This is not valid in liquid phase adsorption, where diffusion of large molecules is slower in narrow pores and this creates the need for the development of wider pores, which will facilitate the entrance to micropores, where adsorption takes place. Experimental or industrial practice have proved that this can be achieved by choosing conditions that favour the development of mesoporous carbons via the pore drilling mechanism. In these applications, the most suitable carbons are those that combine high adsorption capacity and good accessibility [86].

The effect of process variables on pore structure development during activation, has been investigated in the past years. Extensive literature reviews [4,12,31,70,81,87] combined with our research experience [88,89], resulted to the following:

- Technical information and scientific data from literature are mainly based on laboratory work; meanwhile, data from industrial units are scarce, mostly of confidential nature. This creates practical difficulties in designing and operating new commercial units, since up-scaling effects are difficult to be predicted and evaluated.
- Experimental results vary, since they are strongly dependent on feedstock specifications, type of reactor and applied operating conditions.
- Results are also application specific, i.e. the optimum operating conditions are suitable for a specific desired application of the carbonaceous product.
- The primary variable affecting pore structure development is carbon burn-off or conversion degree. Total BET surface area increases at low burn-off values; as burn-off values continue to raise, BET surface area values decrease passing through a maximum value. Total pore volume follows the same trend and in parallel, pore size is increased. When high conversion is achieved, solid structure collapses, resulting to amorphous ash in the end-product.
- Pore diameter depends on the type of activating agent, i.e. reactivity and molecular dimensions. Experimental results prove that pore diameter decreases, under the following order of activating agents ($O_2 > CO_2 > H_2O$); through steam activation the best developed microporous structure is anticipated [70].
- Oxygen compounds are detected in raw material, which can be used to optimize pore structure. In general, an oxygen-rich raw material exhibits a narrower pore size distribution after activation, compared to an oxygen-poor one. In this regard, pre-oxidation of certain raw materials may increase oxygen content.
- The optimum operating temperature seems to be 800–850 °C. A temperature increase, increases reactivity and as a consequence, pore diameter. A partial graphitization of carbon structure during heating, may influence porosity development. Microporosity moreover, is enhanced at higher temperatures. It is also accompanied by high C/H ratios and higher particle densities, due to increased graphitization.

3.4.1. Activation temperature and carbon burn-off
The effect of increased activation temperature on total pore volume seems negligible, while an almost linear increase in porosity is observed as a function of burn-off, at temperatures ranging between 850 °C and 1000 °C. Minor changes are noticed to macropore volume, as well as to already high levels of burn-off above 900 °C; carbon shrinkage probably results to the destruction

of macropores. Micropore volume exhibits high values, at increased activation temperatures. Mesopore volume exhibits higher values at lower temperatures. In conclusion, high activation temperatures lead to the production of a more microporous carbon than low activation temperatures, without influencing the total pore volume created [90]. Two mechanisms of pore volume increase are suggested: (a) pore drilling, leading to a steady increase in pore diameter and (b) pore deepening, leading to porosity increase without affecting pore diameter.

Drilling is the predominant mechanism at low temperatures, whereas pore deepening is favoured at high temperatures [91]. A more detailed description of the mechanism involves three consecutive steps: (a) opening of previously inaccessible pores, (b) creation of new pores and (c) widening of existing pores.

3.4.2. Char particle size

The effect of char particle size on activated carbon porosity development, is associated to pore diffusion and consequently, to the accessibility of the gaseous reactant. In larger particles, diffusion is hindered (low effectiveness factors) resulting in non-homogeneous burn-off and therefore, in a carbonaceous material of enhanced mesoporosity with less microporosity. The opposite is anticipated in the case of chars with high effectiveness factors. The optimal pore structure of the starting char should be bimodal, containing micropores to provide active surface area for reactions and, mesopores and macropores to provide access to the interior of the particle [92].

3.4.3. Residence time

As mentioned previously, the ratio mesopore/micropore volume increases with burn-off depending also on temperature. Generally, long residence times and high temperatures enhance microporosity [90].

3.4.4. Gas phase composition

Char activation, using CO_2 as activating agent, results to enhanced mesoporosity. At 50% burn-off, the meso/micropore volume ratio is 0.69, whereas under comparable conditions during steam activation, this ratio is 0.44 [91]. It seems that the slow diffusion rate of CO_2, prevents the development of micropore structure. Steam activation develops narrow microporosity, whereas CO_2 initially widens microporosity and finally results to a distribution of larger pore sizes [93]. As a general conclusion, CO_2 activation results to lower microporosity and higher mesoporosity than steam.

3.4.5. Alkali additives

Potassium or sodium compounds are added when the desired characteristics of the activated carbon, include either high surface areas and/or increased microporosity. A drastic increase of micropore volume can then be achieved during steam gasification, at comparable operating conditions of temperature and partial pressure [87,94,95].

3.4.6. Type of feedstock

As mentioned previously, accessibility is the primary characteristic of the raw material (pyrolysis char), to facilitate pore diffusion. High surface area values along with high values of mesopore volumes, in conjunction with the relatively high carbon reactivity, so as to obtain high burn-offs in short residence times, are the most important prerequisites of an activated carbon exhibiting high adsorption capacity. On the contrary, the presence of undesired inorganic impurities can block pore structure development, decreasing consequently surface area, micro- and mesopore volumes [96,97].

3.4.7. One-step vs two-step activation process

Preparation of activated carbon via physical activation of chars, takes place in current industrial practice, in two stages: carbonization and activation. It is possible to produce activated carbon in one stage avoiding carbonization. CO_2 as an activating agent was tested in both possible setups; the results indicated that similar yields, micropore volumes and surface areas were obtained, proving that carbonization does not severely affect end-product characteristics [87].

3.4.8. Activation with supercritical water

Supercritical water (SCW) has been employed as an alternative activating agent for the preparation of activated carbon. Compared to steam activation, the use of SCW results in an activated carbon with higher mesoporosity and mechanical strength. Literature findings also concluded that the implementation of SCW can accelerate activation reaction rate, up to 10 times compared to steam activation [87].

4. Activated carbons originated from tyre's pyrolytic char

4.1. Activated carbons from used tyres as received

The production of ELTs-based activated carbons was achieved through a two-stage process: pyrolysis at 400–700 °C and activation at 800–1000 °C [57]. As previously noticed, the type of activating medium, operation parameters and carbon conversion, can influence end product characteristics. For practical purposes, while in parallel aiming to obtain an elevated degree of burn-off, activation temperature is preferred to exceed 900 °C to maintain high reaction rates. Regarding feedstock characteristics, the obtained char yield from ELTs pyrolysis, ranges between 28 and 42 wt%. Moreover, the produced char exhibits low values of adsorption capacity, less than 100 $m^2 g^{-1}$; a negative prerequisite for the following step of activation [27]. The dependence of carbon properties (mainly BET surface areas and porosity) on activation conditions are presented in Table 1, [14,40,59,63,64,81,88,96,98–127]. Ash content in the end product is also a matter of great importance. It has been proved that the reactivity of demineralized (acid treated) char was reduced (22% less) compared to the unprocessed sample [128]. The removal of ash, which previously blocked the pore structure, leads to an increase in micro- and mesopore volumes [96].

Additionally, the degree of burn-off is related to activation temperature, gas pressure and residence time; the burn-off degree is linearly connected to surface area development. High activation temperatures and residence times result in high burn-off values, due to the burn-out of micropore walls [128–130].

In a considerable amount of works regarding ELTs based activated carbons [57], BET values range between 270 and 640 $m^2 g^{-1}$; this is in fact a necessity for end products if the intended use is the production of sorbents for gas or liquid phase applications. Except for S_{BET} values, an additional factor of great importance for the activated carbon production economics, is product yield [131]. High yields improve drastically production economics. The aforementioned carbonaceous products are produced in yields ranging from 7.9 to 34 wt% [57].

However, higher BET surface area values were also noticed (732 up to 1317 $m^2 g^{-1}$); these values characterize samples, as activated carbons able to compete and even substitute commercial products (Table 1). It can be concluded that by selecting the adequate operating conditions, an activated carbon with moderate adsorption capacity but with higher yield, can be produced. The final choice will depend on the specific application and the plant economics. However and based on current technologies and

Table 1
Activated carbon from EOL tyres process: conditions, characteristics and uses.

Process conditions Temperature (T) Residence time (t) Activation agent (AA)		Activated carbon characteristics		Comments	Ref.
Pyrolysis	**Activation**	**yield (wt%)**	**BET (m^2g^{-1})**		
–	$T=900$ °C, $t=3$ h, AA=CO_2	25.6	414	One step process	[98]
$T=600$ °C, $t=4$ min	$T=850$ °C, $t=2$ h, AA=Steam	34.1	528	Product optimum for PAH adsorption	[99]
$T=700$ °C, $t=30$ min	$T=900$ °C, $t=4$ h, AA=CO_2	–	732	Fluidized bed	[81]
$T=500$ °C	$T=850$ °C, AA=Steam	35	985	Good for phenol and dyes adsorption. Char: HCl treated	[100]
$T=800$ °C, $t=1$ h	$T=900$ °C, $t=2$ h, AA=Steam	12.5	1317	–	[101]
$T=800$ °C, $t=1$h	$T=850$ °C, $t=3$ h, AA=CO_2	39	496	–	[101]
$T=500$ °C, $t=2$ h	$T=950$ °C, $t=16$ h, AA=CO_2	33.4	1014	Dye adsorption. Comparable to commercial product. Char: HNO_3 treated	[102]
$T=500$ °C, $t=2$ h	$T=950$ °C, $t=8$h AA=CO_2	18.9	787	Char: untreated	[102]
$T=500$ °C, $t=5$ h	$T=900$ °C, $t=2$ h	–	562	Efficient in Acid Blue 113 adsorption. Mesoporous-comparable to commercial products	[103]
$T=500$ °C, $t=5$ h	$T=900$ °C, $t=2$ h AA=KOH	–	981	Suited for pesticide adsorption. Mesoporous carbon	[104]
$T=500$ °C, $t=5$ h	$T=900$ °C, $t=2$ h	–	562	Suitable for Ni, Pb ion adsorption. Mesoporous	[105]
$T=550$ °C	$T=950$ °C, $t=6$ h, AA=CO_2	–	369	–	[107]
$T=800$ °C, $t=45$ min	$T=950$ °C, $t=2.4$ h AA=Steam	30	472	–	[88]
$T=500$ °C, $t=5$ h	$T=900$ °C, $t=2$ h, AA=HNO_3 treated	–	397	For Aniline derivatives. Mesoporous	[106]
$T=500$ °C, $T=1$ h	$T=900$ °C, $t=1.5$ h, AA=Steam	18 max	530 max	Mesoporous carbon	[108]
$T=700$ °C, $t=1$ h	$T=450$ °C, AA=2% O_2	60	280	–	[109]
$T=700$ °C, $t=1$ h	$T=850$ °C, AA=CO_2	30	660	–	[109]
$T=700$ °C, $t=1$ h	$T=750$ °C, AA=NO	30	460	–	[109]
$T=700$ °C, $t=1$ h	$T=400$ °C, AA=Air	45	300	–	[109]
$T=500$ °C, $t=1$h	$T=850$ °C, $t=90$ min, AA=Steam	–	770	For liquid phase adsorption. Mesoporous	[110]
$T=500$ °C, $t=1$ h	$T=850$ °C, $t=90$ min, AA=Steam Pretreated with $Ca(NO_3)_2$ 500 °C $t=2$ h	–	1000	For liquid phase adsorption. Mesoporous	[110]
Carbon black	$T=900$ °C, $t<2$ h, AA=Steam then treated with Na_2S in liq. and gas phase	–	31–326	Suitable for $HgCl_2$ adsorption	[64]
$T=500$ °C, $t=1$ h	$T=850$ °C, $t=3$ h, AA=Steam	31.4	1177	Steam flow=0.5 g/min	[96]
–	$T=850$ °C, AA=Steam	57	602	ELTs char from low-temperature pyrolysis of waste tires catalyzed by a zeolite	[117]

Table 1 (*continued*)

Process conditions Temperature (T) Residence time (t) Activation agent (AA)		Activated carbon characteristics		Comments	Ref.
Pyrolysis	**Activation**	**yield (wt%)**	**BET (m^2g^{-1})**		
$T=800$ °C, $t=1$ h	$T=800$ °C, $t=2$ h, AA=KOH	58	758	General purpose adsorbent	[111]
$T=500$ °C, $t=2$ h	$T=950$ °C, $t=3$ h, AA=CO_2	20.24	437	Fixed bed reactor, ELTs char treated with 2 N HCl solution at 70 °C, and the solution was stirred for 3 h	[40]
$T=550$ °C, $t=1$ h	$T=500$ °C, $t=2$ h, AA=7% O_2	–	> 80	Post-pyrolysis oxygenation	[120]
$T=500$ °C, $t=12$ h	$T=850$ °C, $t=4$ h, AA=Steam	–	970–1078	ELTs char immersed in HF acid for 24 h. Additionally, chlorination for 1 h at elevated temperatures	[113,114]
$T=550$ °C, $t=2$ h	$T=900$ °C, $t=4$ h, AA=85% CO_2 and 15% N_2	–	186	Medium adsorption capacity of Methylene Blue and Acid Blue 25	[127]
$T=550$ °C, $t=2$ h	$T=950$ °C, $t=4$ h, AA=Steam	–	970	Demineralization with 3 M HCl for 18 h 1/3 char to acid ratio	[127]
$T=600$ °C,	$T=850$ °C, $t=2$ h, AA=KOH	25	398.5	ELTs char washed with 1 M HCl solution and distilled water. Drying at 110 °C for 24 h	[118]
–	$T=935$ °C, $t=6$ h, AA=Steam	35	640	–	[128]
$T=800$ °C, $t=0.5$ h	$T=900$ °C, $t=1–4$ h, AA=Steam	–	240–713	Sulphur modification process: vapour-phase elemental sulphur (S^0) at high temperatures	[63]
$T=550$ °C,	$T=900$ °C, $t=2$ h, AA=Steam	–	272	Activating gas flow rate=485 mL/min	[121]
–	$T=700$ °C, $t=0.5$ h, AA=KOH Ratio (Char/agent 1/1–3/1)	–	951–578	Drying for 24 hr at 100 °C	[119]
–	$T=700$ °C, $t=0.5$ h, AA=NAOH Ratio (Char/agent 1/1–3/1)	–	498–738	Drying for 24 hr at 100 °C	[119]
–	AA=CO_2	–	720	Demineralization with HNO_3/H_2O treatment	[122]
–	AA=KOH	–	242	Demineralization with HNO_3/H_2O treatment	[122]
–	$T=900$ °C, $t=3$ h, AA=Steam	–	996	–	[116]
Pyrolytic ELTs char (Shangai Greenman Eco Science and Technology Ltd.)	$T=800$ °C, $t=3$ h, AA=Steam	–	805.4	Suitable for Malachite Green adsorpion	[112]
$T=450$ °C, $t=2$ h	$T=900$ °C, $t=2$ h, AA=limited air	–	940	Treatment with 1N HCl for 24 h	[124]
$T=450$ °C, $t=2$ h	$T=900$ °C, $t=2$ h, AA=limited air	–	910	Treatment with 1N H_2SO_4 for 24 h	[124]
$T=800$ °C, $t=6$ h	$T=900$ °C, $t=2$ h, AA=Steam	–	465	The produced activated carbon is further subjected 4 M nitric acid solution to remove the ash content	[123]
$T=680$ °C, $T<0.01$ h	$T=1000$ °C, $t=3$ h, AA=Steam	9.5	620	Activating gas flow rate=148 mL/min	[14,59]
$T=800$ °C, $T=0.75$ h	$T=900$ °C, $t=2$ h, AA=H_2O–CO_2	9.5	358.5	Activating gas flow rate=758 mL/min	[125]

literature data, ELTs char activation temperature is proposed to exceed 800 °C [57,132].

The most common activating agents for physical activation of ELTs pyrolysis char, are steam or CO_2. During steam activation, pores are broadened and their adsorptive capacity raises; micropore volume also increases [133]. Initially, ELTs chars develop a very narrow microporosity followed by a continuous pore enlargement, transforming microporous structrure to more mesoporous, at higher residence times [134]. On the other hand, surface area development during CO_2 activation, is not severely affected by particle size and elevated temperatures, in the range of 950–1100 °C [102,135]. Moreover, experimental data depict that

Table 2
Commercial activated carbons general characteristics.

Product	Uses	Raw material	Recyclable	Price ($/cbf)	Ref.
Filtrasorb 200	Taste and odour compounds removal,	Bituminous coal	Steam,	~200	[145]
Aqua Nuchar®	Water treatment	Wood	n.m.	15.3	[147]
UltraCarb® 1230AWC	Drinking water treatment	Coconut shell	Yes	65	[148]
Hydrodarco 3000	Water treatment applications	Lignite coal	n.m.	32.1	[146]
Aquacarb 830AW/ 1240AW	Pesticide removal	Antracite coal	Yes	80	[148]
VOCarb® P60 and P70,	VOC control from air strippers	Anthracite coal	Yes	~140	[148]
VOCarb® 46 and VOCarb® 410,	Solvent recovery of low b.p. solvents	Bit. coal		~140	
VOCarb® 410 HgFree and VOCarb®	Mercury removal	Bit. coal		~140	
VOCarb® 48C,	Vapour phase treatment	Coconut shell		~295, ~140	
MIDAS® Odour Control Media (OCM),	High VOC adsorption capacity	Bit. coal			
410 LoRise/ P60 LoRise	Industrial vapour control system	Bit./anthracite coal			
PICAGOLD® G210AS,GoldSorb® 5500	Gold recovery operations	Coconut shell	n.m.	n.m.	[149]

CO_2 at a higher partial pressure can increase surface, while the opposite trend is detected when increasing residence time (micropores are minimized, while at the same time meso- and macropores are developed) [129,136,137]. In the case of ELTs char activation with CO_2, the resulting carbon exhibits lower micropore volume than in steam activation at higher burn-off (> 40%) [102]. In general, as water molecules are smaller than those of CO_2, steam-prepared activated carbons exhibit higher BET surface areas than those prepared through carbon dioxide activation, even exceeding the value of 1000 $m^2\,g^{-1}$ [93,129,133,134].

Alternatively, ELTs char characteristics can be upgraded through chemical activation. Chemical activation is conducted under lower temperatures and in most cases, KOH was selected as activation medium. The exhibited surface areas values of the produced activated carbons, range between 242 and 981 $m^2\,g^{-1}$, Table 1 [94,111,119,122]. Literature findings also highlight that, surface area and total pore volume increase when more KOH gets impregnated (maximum achieved at a 4/1 ratio of KOH/tyre, w/w [94]).

Numerous experimental attempts during the past years, aimed towards the production of carbonaceous products able to adsorb specific substances, mainly liquid-phase pollutants. Pores of different sizes can exhibit individual characteristics; however, as a whole they are contributing to the adsorbent's overall capacity. The presence of micro- and especially mesopores in activated carbons, enhance the adsorption of large adsorbates, even dye molecules [138,139]. Some authors have modified ELTs based activated carbons to tailor properties for the adsorption of various pollutants. More specifically, carbonaceous adsorbents were developed as adsorbents for Cd^{2+} in aqueous solutions, methoxychlor, atrazine and methyl parathion in waste water, copper and p-nitrophenol, p-chlorophenol in aqueous solutions and Ni^{2+} from synthetic solutions and metal fabricating industrial wastewater [140–142].

4.2. Activated carbon from pyrolytic char of de-mineralized tyres

There are few studies regarding the activation of demineralized ELTs, possibly due to the high cost included (pretreatment of ELTs and a consequent intensive washing are required), Table 1. Literature findings proved that the lower reactivity of demineralized ELTs chars exhibited when activated, might be attributed to the presence of inorganic compounds (Ca, Zn, etc.), which appear to have a catalytic effect to the activation process [96,97]. As expected, the removal of undesired inorganic impurities, led not only to an increase of surface area values but also, to increased micro- and mesopore volumes. Furthermore, the exclusion of inorganic impurities from tyre char, such as inorganic oxides and sulphur, assure a variety of possible applications by minimizing undesired environmental impacts (gaseous emissions/liquid contamination). Therefore, this could be proved a sound solution to solve both the wastewater treatment problem and the waste tyre stockpiling problem [97,126,128,143].

4.3. Activated carbon applications

Activated carbons are mostly biomass based; literature findings indicated that adequate precursors for activated carbon production could be: corn cob, olive, apricot stones, cherry stones, almond and nut shells, rice husk/straw, etc. [144]. However, used tyres can also be used towards that direction. Based on specifications of commercial activated carbons, the end-product of an ELTs char activation process, should at least fulfil some essential qualifications in order to be efficiently marketed. More specifically, the prerequisites for an activated carbon, based on market criteria, are iodine number > 500, moisture content < 10 wt%, ash < 10 wt%, mean particle diameter > 0.5 mm, ignition temperature > 350 °C, apparent density 0.3–0.7 $g\,ml^{-1}$, hardness number > 85 and molasses number > 50. Moreover, activated carbons should be able to be produced in either powdered, granular or pelletized form. In Table 2 some indicative commercial activated carbons are presented along with their most important properties [145–149]. Apart from the more conventional uses of activated carbons (depollution applications), more innovative uses of these carbonaceous materials include catalyst support, supercapacitors electrode material, hydrogen storage materials, manufacturing of cloth and gold extraction applications; the precursors of those materials are coal or biomass based [150,151].

4.3.1. Gas phase applications

Activated carbons for air purification processes were designed to meet specific customer objectives through a wide variety of applications, including flue gas decontamination, odour removal for sewage treatment operations, NO_2 removal, acid and corrosive gases (H_2S & SO_2) removal, formaldehyde capturing, etc. [97,152,153]. Furthermore, activated carbons provide an effective means for gas phase applications, such as separation, storage and catalysis of gaseous species. Adsorbed Natural Gas (ANG) technology enables the efficient storage of natural gas [154]. Additionally, other flammable gases (e.g., acetylene) can similarly be stored under pressure.

Based on the characteristics of the corresponding commercial products, the majority of the above mentioned applications can be fully performed by ELTs based activated carbons [57]. Activated carbons may be used efficiently for air pollutants control, during flue gas treatment. During the adsorption of SO_2, a tyre based activated carbon exhibited an adsorption rate similar to a commercial, lignite-based, carbon [153]. Moreover, ELTs based steam activated carbons were successfully used in naphthalene adsorption (a PAH model compound); their adsorption capacity was increased 2000% compared to ELTs pyrolysis char [99]. A tyre based activated carbon was also found superior regarding mercury

Table 3
Comparison of waste tyre based activated carbon production cost to biomass derived activated carbon.

Type of Raw material	Activation method/agent used	Plant product capacity (kg day^{-1})	Production cost ($kg^{-1})	Ref.
Used tyres	Steam	4500	1,72	[174]
Used tyres	Steam	4500	2.23	[131]
Used tyres	KOH	4500	1.92	[131]
Pecan shell	Steam	1370	2,78	[168]
Pecan shell	H_3PO_4	4900	2,89	[169]
Almond shell	H_3PO_4	5000	2,54	[170]
Almond shell	Steam	2180	1,54	[171]
Bamboo waste	KOH	6600	1.3	[172]
Sugarcane bagasse	Steam	1940	3,12	[168]
Poultry litter	Steam	3358	1,44	[173]

Table 4
Activated carbon prices.

Year	Country	Price ($kg^{-1})	Shape	Application
1995	USA	1.65–9.9	Granular	General use
1995	USA	0.8–2.0	Powdered	General use
1995	Europe	0.7–1.5	Powdered	Water treatment
1995	Europe	1.4–5.0	Powdered	Food, pharmaceutical
1995	Europe	1.6–1.75	Granular	Water treatment
1995	Europe	2.5–5.0	–	Gas phase
1995	Europe	4.0–6.0	Extruded	–
2003	–	3.3[a]	–	General use
2003	–	4.0–5.0	–	Specific
2003	–	20.0	–	Metal ion adsorption
2004	–	1.92[a]	–	General use
2005	China	0.82	–	General use
2005	Japan	3.11	–	General use
2005	USA	1.93	–	General use
2005	Philippine	1.432–1.628	–	–
2005	India/Indonesia	0.655–1.136	–	–
2006	Europe	1.52	–	General use

[a] Imposed by production cost

adsorption, in comparison with a coal-derived activated carbon or even with commercial products [100,125] In another study, the activated ELTs char was used as a catalyst for tar destruction during biomass pyrolysis. The results indicated increased efficiency that exceeds 98% as well as benzene production in the producer gas; however due to the endothermic characteristic of the process additional energy is required [155].

4.3.2. Liquid phase applications

ELTs based activated carbons can be also used in liquid phase applications including, water purification, removal of organics (including phenolics and aniline derivatives), dyes (Acid Blue 113, methyl orange) and heavy metals (chromium, nickel ions, lead and uranium) removal, [103,105,106,110,123,142,156–160]. Based on experimental findings, a tyre based activated carbon was found superior regarding mercury adsorption, in comparison with a coal-derived activated carbon or even with commercial products [64,100,125]. Additionally, activated carbons in liquid phase applications are used to improve taste, smell and colour, including removal of chlorinated compounds and other VOCs [141]. Activated carbons represent a key element to the quality improvement of both ground water and aquaria water, but also to household water purification.

Additionally, activated carbons are also utilized in industrial applications including mining operations that require water-treated supply, metallic ion adsorption (gold and other metals), and adsorption of excess flotation reagents. Furthermore, food, beverage and oil industries use activated carbons to remove colour and unacceptable tastes (e.g., the sugar and sweetener industries need decolourization agents during the production of white sugar) [161]. Activated carbons also represent an essential part of various processes in pharmaceutical production, including purification of process water and use on fermentation broths.

However, up to date ELTs based activated carbons have been successfully used to purify industrial wastewaters containing Pb, Ni^{2+}, Cr (III), Cd^{2+} and even pesticides [64,104,105,142,160,162,163]. Moreover, toluene adsorption was also achieved when ELTs based steam activated carbons were used; the experimental results proved their superiority over commercial activated carbons [113,114].

5. Economic viability and LCA

Recent statistical studies have concluded that the demand for activated carbons, including virgin and reactivated products, is

expected to rise significantly. During the following years a major increase is anticipated for industries, due to the stricter mercury removal standards applied. In value terms, the activated carbon market only in USA, will reach $1.35 billion. This increase will also originate from the broadening of available applications that enable the use of activated carbons [164]. Since ELTs based activated carbons are still excluded from that market, there are great financial potentials regarding a possible realization of an endeavour that produces carbonaceous adsorptive materials using as precursors ETLs; meanwhile this could strengthen efficiently, plant's viability. However, the high levels of ash and metals, as a result of their manufacturing process should be properly addressed, especially if targeted to environmental remediation applications.

Activated carbons selling price depends mostly on its quality (adsorption capacity and adsorbate type) and less on product yield. Raw material cost, plant capacity and activation route represent additional key-points for plant economics. However, the selection of a large capacity production unit, can provide attractive economic figures on one hand, but also pose problems in small markets, on the other. The conduction of an analysis, starting with a plant capacity calculated at the break-even point, is recommended [131].

5.1. Manufacturing cost

Despite the fact that activated carbons can be used in a wide range of environmental depollution applications, their widespread use is also restricted due to high associated costs [165]. However, the valorization of low-cost precursors for activated carbon production can surely benefit industrial-scale endeavours [166,167]. There are few data and studies related to activated carbon manufacturing cost (Table 3) [168–174]. The range of activated carbon selling prices, across the globalized market varies. There have been reported prices as low as 0.6$ kg^{-1} (Asian countries-no specs) and as high as 25 and even 38$ kg^{-1} for special uses (pharmaceutical), Tables 4 and 5. An average indicative price for ordinary application seems to be about 7$ kg^{-1}, Table 6. In many techno-economic analyses authors accept as safe selling price, 2$ kg^{-1}. In parallel, manufacturing costs in the same studies range between 1.1 and 3.2 $ kg^{-1} [131,168–174].

5.2. Selling Price

The market price of activated carbons varies, as it is a complicate equation of demand, product quality, production cost,

Table 5
Bulk Granular activated carbon selling prices (2012).

Code	Raw material	Activation method	Iodine number (mg g^{-1})	Use	Price in \$kg^{-1}
Aquarium AC	–	Steam	–	Fish aquarium	7.0
GAC610	Coal	Steam	Iodine/1000	Water purification	7.0
Coconut, varying mesh	Coconut	–	Iodine/1000	Air/vapour	5.7–7.5
GAC2050,Spartan	Coconut	Impregnated modified	Iodine/1050	Sulphide, chloramine	12.3
Calgon F-200	–	–	–	–	7.6

Table 6
Bulk Powder Activated carbon selling prices (2012).

Code	Raw material	Activation method	BET surface area (m^2 g^{-1})	Use	Price in \$kg^{-1}
CD-325C	Bamboo	Steam	> 1100	Chemical/Pharmaceutical/Food	25.3
ACPI1250C	Coconut	Steam/acid washed	> 1500	Medical	18.3
USP8325C-AW	Coconut	Steam/Acid washed	> 1450	Medical	16.7
ACP-1500	Hardwood	–	2000–2400	Medical	8.5
ACP-SA20	Hardwood	–	1400–1800	Chemical/pharmaceutical/food	7.7
Norit A Supra	–	Steam	1700	Chemical/pharmaceutical/food/antidote	83.0
Norit SA4	–	Steam	800	Decolorization	13.7
PAC-325	Coal	Steam	–	–	4.9

Table 7
Activated carbons wholesale prices from Chinese suppliers (2013).

Shape	Raw material	Application	Minimum quantity (tons)	Price, \$(metric ton)$^{-1}$
Powder	Coal	Water purification	10	700–1800
Powder	Nut shell	Coating auxiliary agents, water treatment chemicals	10	500–1800
Powder	Coconut shell	Chemical auxiliary agents	10	1200–2000
Powder	Wood	Sugar decoloring air purify and water purify	100	200–500
Powder	Bamboo	Coating auxiliary agents, Leather auxiliary agents, Paper chemicals, Petroleum additives, Plastic auxiliary agents, Rubber auxiliary agents, Surfactants, Water treatment chemicals.	1	1500–1800

etc. [87]. Certain characteristics can determine the selling price (granular carbons for wastewater treatment can be up to three times more expensive). However, the prices of granular and powdered activated carbons for gas and air purification processes, are, in most cases, similar. In Europe, activated carbon prices vary, due to the large number of grades and qualities available. The intense price fluctuation noticed during the last 20 years in Europe, resulted in higher current selling prices in Europe than in US market.

In Tables 4 and 5, the actual prices (2012) of commercial activated carbons are reported. Granular carbon prices range between 5 and 12 \$ kg^{-1} with an average price of 7\$ kg^{-1}, presenting a low variance in price depending on the utilization route [145,146,175].

Powdered carbon products are more expensive in this case; prices vary considerably according to application. Prices can be as low as 5\$ kg^{-1} and in an extreme case as high as 83\$ kg^{-1} for a specialized application. Among them, carbons with a selling price of 7, 18 and 25 \$ kg^{-1}, according to the proposed use, were also noticed. The above prices represent values for small quantities (retail prices); one has to consider that prices for large quantities should be much lower, roughly the half. China is considered to be among the most important producers of activated carbon. Indicatively, Chinese activated carbons wholesale prices are presented in Table 7. Prices vary between 0.2 and 1.8\$ kg^{-1} for quantities above 1 t, depending on the proposed use of the final product [176–180].

5.3. Life cycle assessment

Aiming to improve process design while achieving a multi-objective optimization of processes, Life Cycle Assessment (LCA), has become a valuable tool which can be applied either as a standalone tool, or combined with other environmental assessment tools, to evaluate products, services, Environmental Management Systems (EMS), environmental policies and processes [181,182]. The structure of a LCA consists of four distinct phases: (1) Goal and scope definition, (2) Life Cycle Inventory analysis (LCI), (3) Life Cycle Impact assessment (LCIA) and (4) Life Cycle Interpretation [183]. The experimental data exported through completed operations (mass and element balances), can fully supplement the necessary input for LCA [184]. However, additional information are needed, including energy consumption of the process, bills and stock-inventory changes on consumables, emission measurements, pollutants concentrations, off-gas and waste-water amounts and finally, wastes and products composition [38].

The environmental impact associated with activation of carbonaceous materials strongly depends on the precursor materials used, along with the type of activation processes applied (operating conditions, activation medium). An extensive bibliographic review, regarding the LCA of ELTs management options [182,185–187] resulted to poor findings [188]. Moreover, the subject of the present study, the activation of ELTs derived pyrolytic char, is not included in any of the previously reported LCA studies. On the other hand,

the environmental impact of the production of activated carbons suitable for environmental depollution applications, through physical or chemical activation, from conventional precursors (hard coal) or biomass waste materials (olive waste cake), was reported in literature.

Hjaila et al [189] in his study identified that chemical activation through H_3PO_4 is responsible for a high environmental impact. Eutrophication, terrestrial ecotoxicity and fresh water aquatic ecotoxicity were severely influenced. The overall use of this activation agent was also found responsible for high environmental impact during washing of the end product. The CO_2 emissions during the production of 1 kg AC were calculated to 11.096 kg whereas the electricity needed, did not exceed 3.13 kWh/kg AC produced. Gabarell et al. on the other hand, using as precursor hard coal, physically activated the pyrolytic char. The calculated values, indicated similar levels of CO_2 emissions during activated carbon production, but also lower levels of contribution to other impact categories, as compared to chemical activation [190].

The comparison of these activation methods depicts the advantages stemming from the use of physical activation over chemical, majorly due to the increased environmental impact originated from the use of H_3PO_4. Due to the variety of activating mediums though, new studies are required to contribute more to the schematization of an overall critique based on sustainability

Table 8
ELTs pyrolysis technology of pilot and industrial scale. General characteristics and main obstacles occurred.

ELTs pyrolysis technology	Operational conditions		Advantages	Main obstacles	Ref.
	Temperature (°C)	Flow rate (kg h^{-1})			
Thermomechanic-cracking pilot scale reactor	500	10	• High yields of char and liquid. • Char as a solid fuel or activated carbon precursor and • The gas as make up heat source or electricity production	• Pyrolytic liquid of high sulphur content and low Cetane Index; it is usable up to 40% in mixtures with diesel oil • Alternatively, it is preferred to be used in stationary and marine diesel engines	[22]
Continuous auger pilot plant (moving bed reactor)	600	8	• Decreased reaction time • Gas combustion can cover energy needs of pyrolysis • Pyrolytic liquid can be used in mixtures with common diesel oil • Stable char yields	• Pyrolytic liquid needs refining (desulfuration). The untreated oil when combusted, results to higher smoke opacity and higher CO, NO$_x$ emissions	[16,17,21]
Several fixed bed reactors in parallel	700	12	• Increased gas, liquid and char GCVs (64–83 MJ N^{-1} m^{-3}, 41–43 MJ kg^{-1}and 27–28 MJ kg^{-1}, respectively) • Legislation approves the use of tyre pyrolysis oil in mixtures up to 4% in mixtures with diesel oil	• High ash and zinc content in the produced solid	[23]
Two batch horizontal rotary kilns	420	4500/batch reactor	• Gas heating value exceeds 37 MJ kg^{-1} • Pyrolytic liquid (GCV) in the range of 42 MJ kg^{-1} • The produced char can be used as a solid fuel, activated carbon, printers ink	• Continuous monitoring and consultancy is necessary regarding: Raw material quality, management of the produced gas and liquids, SOx and dioxin emissions, wastewater treatment. • Pyrolytic liquids should be upgraded through environmental friendly processes	[24]
Rotary kiln thermolysis plant	500	650	• Versatility in raw materials • Optionally, distillation and desulphurization departments can be attached increasing plants versatility	• The venturi-washer adds significant operational cost to the investment	[20]
Rotary kiln pyrolysis	n.m.	< 50	• Non-problematic operation • Valorization of pyrolysis products	• Not yet applied. • The desired size of ELTs particles should not exceed the following dimensions: 3∗3 cm^2 or 1.3∗1.3∗1.3 cm^3. • ELTs particles should be free of stones, glass, metals. • ELTs particles should have a calorific value of 18 MJ kg^{-1}. • The maximum capacity should not exceed 50 kg h^{-1}	[18]
Biogreen Spirajoule	< 900	2000 h^{-1}	• Energy efficiency ratio up to 91%. • The produced oil is similar to No. 2 heating oil. • The produced gas and char can be used for electricity production and as a carbon black, respectively	• High values of sulphur in the received solid 2.8 wt% • ELTs particles should have low moisture content and a particle size less than 20 mm are prerequisites for a safe operation.	[19]

criteria. The results from a Life Cycle comparison between several activated carbon preparation processes can indicate economic and environmental burdens that might discourage the adoption of a certain technology. These results can be used also to inform policy makers, for any moral and legal issue that may occur, assisting effectively to its immediate and successful solution [188,191].

5.4. Scaling up ELTs pyrolysis system

The scientific advances in ELTs pyrolysis have drawn a detailed scheme regarding their potentials. Several approaches towards the effective valorization of ELTs have been made. The majority of them refers to pilot scale operations. In Table 8 the current problems noticed from operating waste-tyre pyrolysis plants (pilot and industrial scale) are presented along with their most important characteristics.

More specifically, ELTs pyrolysis was performed in an innovative pilot scale pyrolyser (US patent No. 20100008836). The pyrolysis unit consisted of a thermo-mechanic cracking reactor designed as a twin-screw extruder with decreasing section, realizing mixing and mechanical pressing of ELTs. The setup offered the advantage of a non-problematic collection of products [22].

An analogous effort regarding ELTs pyrolysis of pilot scale, included a continuous auger pilot plant which consisted of four main parts: the feeding system, the reactor, the vessel for solids collection and the condensing system. The proposed process was tested on a continuous operation of 100 h, at temperatures that did not exceed 550 °C in mass flow rate of 6.7 kg h^{-1} for a small residence time (3 min). The produced gas can be used to cover the energy needs of pyrolysis process (power generation and/or thermal applications). Moreover, CO_2 emissions proved to be significantly lower than those emitted from direct waste tyre combustion. They were also less than those occurred from conventional fossil fuels combustion, for electricity generation [16,17,21].

Another semi-batch pilot plant consisting of several fixed bed reactors, arranged in parallel, was also used to pyrolyse ELTs. The produced gaseous products were directed to gas turbines, for electricity production (4.1–6.5 kWh (kg of ELTs)$^{-1}$). Regarding pyrolytic oil, a large increase of PAH content was noticed at temperatures above 550 °C, while the content on monoaromatic compounds, remained practically constant, over the studied temperature range.

The produced oil could be used as a fuel, since the local legislation permitted pyrolysis oil–diesel oil mixtures, up to 4% by weight (DOGC 2166/1996, Decreto 34/1996). Finally, the solid product due to its high ash (17–21 wt%) and zinc content, should be primarily processed prior to valorising, for adsorptive materials production [23].

The first small scale commercial tyre waste pyrolysis plant has been installed in Bangladesh, by the Radiant Renewable Energy (RRE) Ltd. at Gazipur, Dhaka. The characteristics of the obtained pyrolysis products were found comparable to literature findings [24]. Another industrial scaled tyre pyrolysis plant was installed in Cyprus; the unit included a rotary kiln thermolysis plant, a turbine, an off-gas cleaning apparatus. The main problem which had to be addressed occurred through the installation and operation of venturi-washer [20].

Additionally, there is a number of manufacturers that tend to facilitate, at full extent, the construction and operation of an ELTs pyrolysis plant especially of pilot scale; these facilities are mostly targeting to trials and development [27,192]. Prior to commercialization, pyrolysis of ELTs should fully address several issues regarding legislation, emissions, standardization of products, while optimizing of the structural and operational process parameters [182].

An Irish company, which aims to develop a depolymerization process of ELTs, through pyrolysis, promoted the use of a pilot

scale rotary kiln. A non-problematic continuous operation could be achieved under certain specifications, regarding mainly the raw material [18]. Another manufacturer, Biogreen® via spirajoule technology, aims to perform ELTs pyrolysis at temperatures up to 900 °C at a maximum capacity of 2 t h^{-1}, resulting in valuable products [19].

EU along with the corresponding legislation, aims to efficiently deal with the problem of ELTs management. For this reason several research programs have been financed, targeting to develop innovative ELTs management methodologies. Regarding ELTs thermochemical valorization, apart from the previously described DEPOTEC project, TYGRE project was also financed [26,193]. TYGRE aims, through gasification, to recover high added-value products from selected waste streams (ELTs); as stated by Waste Framework Directive, ELTs can constitute a part of waste streams. Their management is proposed to follow certain methodologies, under the assumption that ELTs full comply with End of Waste criteria [194,195]. The potentials that ELTs gasification provides, are investigated through the coupling with a second thermal process, aiming ultimately to the production of ceramic materials [193].

6. Dual hybrid system barriers and recommendations for successful implementation

6.1. Complexities and obstacles

A combined process that aims to enhance the viability of ELTs pyrolysis would certainly encompass a hybrid dual system, targeting either to the production of activated carbons or to the electricity production. Due to the complex nature of the proposed process, several obstacles may occur. These are mostly related to the quality of the received products. Purification processes for gas and liquid products are essential in order to ease their effective valorization.

A hybrid system should include adequate burners for pyrolytic gas, with an attached filtering system to reduce the HCl and SO_2 concentration; in these cases, acid gas, water or a column packed with activated carbon can be used. The desired outcome should guarantee that the produced emissions fully conform to the limits proposed by Waste Incineration Directive [196]. An apparatus addressing the above issues, includes a TOTEM® electric co-generation turbine (Total Energy Module) consisting of a distillation gas-fed 903 cm^3 engine coupled to an engine/alternator accompanied with an electronic coupling system. The generated electricity can be consequently distributed to the local electricity network [197].

Regarding the quality of the liquid product of pyrolysis, literature findings indicate the most crucial characteristics that should be addressed. The liquid product should be homogenous, filtered, with a low water content sustaining a single phase structure; this would permit its non-problematic storage for a significant amount of time. This is a crucial parameter, since aging tests have proved an undesired increase of viscosity [198]. To minimize the undesirable properties of the produced pyrolytic liquid, the mixing of the liquid fraction with commercial diesel oil is proposed. The obtained results are satisfactory, allowing a safe operation for I.C.E. and motor engines [17,49–51].

Towards minimizing the depletion of fossil fuels, ELTs pyrolysis oil can be used, partially or as a whole, as a liquid fuel. 1.75 million tons of pyrolysis oil can be produced per year substituting less than 0.6% of the oil consumed annually to EU for transportation needs [22]. However, additional work has to be done to address appropriately, the higher sulphur content and higher aromatic content, as compared to commercial fuels [53].

Aiming to the above scope, the pretreatment of pyrolysis oil (including filtering and desulfurization) prior to its mixing with common diesel oil, would assure better results regarding, exhaust emissions and maximization of the engine performance [50]. ELTs pyrolysis oil with improved characteristics, regarding reduced aromatic and olefinic content, can also originate either from the co-pyrolysis of ELTs with oily wastes from ships (bilge water oil and oily sludge) or from co-pyrolysis of ELTs and biomass [53,199].

Finally, the solid product, as stated above, should be an adequate precursor for its efficient valorization towards the production of activated carbon, or other carbonaceous products with adsorptive characteristics. The resulted char from ELTs pyrolysis, apart from the desired high ratio of C/H, exhibits undesired high percentages of sulphur and ash. Scientific studies have proved that elemental sulphur during pyrolysis is mostly distributed to the solid product of pyrolysis; this could endanger the suitability of the produced adsorptive material, regarding its intended use on environmental depollution applications [200]. Ash, on the other hand, can be easily removed in environmental friendly processes. De-mineralization of the produced pyrolytic char can be achieved by the use of acids (HCl, H_2O_2, HNO_3 and H_2SO_4) and base NaOH. This can ultimately lead to improved surface and structural characteristics of the produced adsorbent [34,96,126,129,162,201,202].

6.2. Recommendations for an integrated dual scheme of pyrolysis/activation process

An activated carbon plant should be part of the integrated tyre pyrolysis-activation production complex. The main purpose should be the production of a high added value material that will provide the plant with satisfactory total income, taking under consideration product's marketing and commercialization concerns, which were previously mentioned [131].

There are two strategic technological choices in this regard:

6.2.1. A large capacity-continuous double kiln operation plant

This choice is preferred when large demand for activated carbon product is anticipated by marketing previsions. 24 h per day – 355 days per year operation is anticipated, while plant capacity should be imposed by product demand. Pyrolysis oil after its separation from gas should be stored provisionally in a tank; next, it will be valorised as fuel to cover the energy needs of the activation kiln. Pyrolysis char should be stored in a silo and subsequently fed to the activation furnace. The process consists of the following sections shown in Fig. 4:

- Tyre-char storage silo and feed-in system consisting of screw feeders, star valve and conveyor. The system is capable to supply solid feed to the activation kiln at a constant rate, under airtight conditions.
- The co-generation unit that supplies the activation steam (Heat Recovery Steam Generator) which is subsequently preheated to a heat recovery exchanger (economizer) and fed to the activation kiln [38].
- The rotating kiln. Most frequently, it is indirectly heated and it can be equipped with pyro-oil burner(s).
- The activated carbon product draw-off, cooling, conveying, storage, packaging and track-loading system.
- The pyro-oil storage and supply to the kiln and to the co-generation unit of the system.
- The flair to which activation off-gas is directed after cooling in the economizer. The flair is also an end point for the flue gas emitted from pyrolysis oil combustion, after desulphurization

(primarily in an adsorption column and secondly in an activated carbon column).

6.2.2. A medium capacity-batch one kiln operation plant

When market research shows a small demand for carbon product, a *single kiln* would be preferable, in an intermittently (batch) operated plant. At first, plant will operate for pyrolysis of ELTs. The produced oil and char will be stored and should be available for the second stage of activated carbon production. A production schedule should be necessary for a rational plant operation. This operating mode has a lower investment cost by about 30% due to the employment of one kiln only. In addition, the selection of low cost equipment providers-constructors is another way, often underestimated, that can decrease plant cost. *This scenario is also proposed in the present study*. The proposed process consists of the same sections of the previous scenario, with the difference of processing both pyrolysis and activation, in one kiln.

For both strategic scenarios, pyrolysis oil can be used as fuel in the activation kiln and in the cogeneration unit. A boiler is needed to produce high pressure steam; following, it is fed to a steam turbine for electricity generation. Low pressure steam from the steam turbine will be then supplied to the activation kiln and other users [38]. Any excess electricity may be sold to the local power company. Based on the above, the proposed process can achieve the following (Fig. 5):

- It has a strong economic incentive since it produces a marketable, high-added value product.
- It is energetically self-sufficient and furthermore, it can generate electricity, which can be provided to the local network, thus improving ELTs pyrolysis plant economics.
- It has a minimum environmental impact, well within acceptable standards.

Therefore, one can conclude that this is an improved ELTs pyrolysis scheme and a competitive disposal option for used tyres. Attention however, should be paid in some drawbacks, such as the necessary licences required for using by-products as fuels and carbon product suitability for specific applications.

6.2.3. Continuous conical spouted reactor technology

Another attempt to increase ELTs pyrolysis process viability encompasses the use of a conical spouted bed reactor (CSBR). Its advantageous hydrodynamic characteristics assure efficient heat transfer between phases in the spouted bed. Furthermore, its geometrical characteristics offer a versatility in gas and solid flow-rates under stable and isothermal conditions in the bed. This technology offers flexibility on raw material selection, in a continuous operation, while assuring stability for char yield and its characteristics, targeting simultaneously to maximize the yields of gas and liquid hydrocarbons [203–207]. A conical spouted bed reactor in a continuous operation can produce high yields of limonene and gases, while providing flexibility in the operating conditions and ease at the continuous removal of the residual pyrolysis char [205]. The adulterated pyrolysis char obtained is of limited quality, given its relatively low surface area values (> 120 m^2 g^{-1}). In order to use this solid residue as activated carbon, an activation process with steam or carbon dioxide is required. There are encouraging results for the valorization of pyrolysis char obtained by tyre pyrolysis, which is a subject of increasing interest in view of the good performance of activated carbons, obtained from residual materials, in environmental applications [205]. The produced pyrolytic oil can be used in I.C.
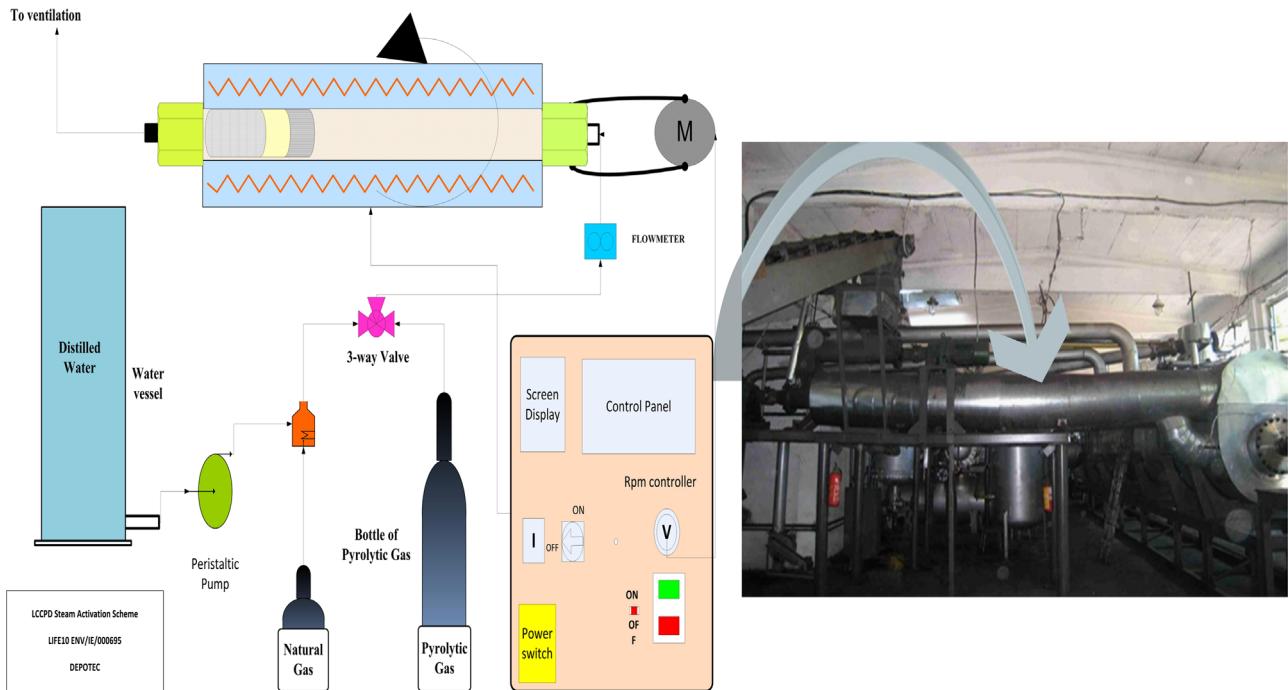
Fig. 5. Integrated Flow Sheet and conception of activated carbon production from ELTs.

E., if subjected to mild hydrotreating operations that will reduce its viscosity and aromatic content [45].

Moreover, the implementation of a catalyst, in the same reactor, resulted in high yields of highly aromatic content. An FCC catalyst increased the yield of diesel fraction, from 9 wt% at non-catalytic pyrolysis, to 50 wt%. Therefore, so as to meet commercial fuel standards, the obtained pyrolysis liquid is proposed to be subjected to hydrotreatment processes [208].

However, the continuity regarding ELTs char valorization, included an additional fixed bed reactor for the production of activated carbons, using either steam or carbon dioxide as activation agents, at 850 °C and 900 °C, respectively. The produced activated carbons exhibited a mesoporous structure, with BET surface areas above 500 $m^2 g^{-1}$ and 370 $m^2 g^{-1}$ for those obtained using steam and carbon dioxide, respectively; the end-product is suitable for adsorption of compounds of a large molecular size. It is also worth mentioning that under steam activation, sulphur was more efficiently removed from the char during activation, a desirable characteristic for a solid carbonaceous material targeted either to adsorptive environmental depollution applications, or alternatively, to tyre manufacturing [209]. The above justify CSBR's stability for various operations, apart from ELTs pyrolysis, including coating, drying and polymerization processes [210]. However, serious issues should be addressed regarding inter-particle forces, particle deformation and compression, intra-particle moisture migration and jet dynamics at the entrance [211].

6.3. Recommendations for decreasing pyrolysis cost

The preferable process conditions would certainly aim towards a profitable production of adsorptive carbonaceous materials. For instance, a manufacturing cost of 1.5–1.7$ kg^{-1} would be acceptable (Table 3). It is to mention that the price of 2$ kg^{-1}, corresponds to wholesale price. According to market practices, this price can be almost tripled for the consumer (retail price), reaching 6$ kg^{-1}; this is in fact a price that compares favourably with that of 7$ kg^{-1} mentioned earlier.

Considering the worst case scenario and the data presented in Tables 3–5, 6$ kg^{-1} is quite high compared to 0.6–2.5$ kg^{-1} of minimum retail prices. Based on the above information, it is reasonable to accept a retail price for a typical activated carbon of 2$ kg^{-1}, which in turn results to 0.66$ kg^{-1} (one third) maximum selling price for the manufacturer. Accepting a 30% margin as a profit for the manufacturer, a final, safe and realistic minimum manufacturing cost results to be 0.46$ kg^{-1}. This cost is significantly lower than 1.6–2$ kg^{-1} used in the above mentioned economic analyses.

Consequently, manufacturers have to increase their effort to reduce manufacturing costs taking under consideration the following important recommendations:

6.3.1. Reduce raw material cost as low as possible

It is advised to select a raw material of low cost or even free of charge. In case of ELTs, their state (whole or shredded) is the key parameter to their procurement price. Additionally, mixtures of low and high quality feeds are another attractive possibility [53].

6.3.2. Minimize plant capital cost

Plant costs reported in literature often are unduly high. Since activation equipment is practically custom-made, the selection of a small construction company may be preferred. Low-labour cost countries may be an attractive choice.

6.3.3. Good choice of Carbon product properties

They should be tailored to a specific application, as requested by customer under the analogous pricing criteria.

6.3.4. Application of energy conservation technologies

This is a critical action since activated carbon production is an energy intensive operation. High temperature waste streams can be valorised to reduce the energy demand of the process.

6.3.5. Use of one step production scheme

Pyrolysis and activation process can be both applied in the same reactor.

6.3.6. Plant capacity

Maximization of capacity should be targeted.

6.3.7. Operation mode

Batch operation seems more suited for small plants but continuous has some advantages.

6.3.8. Automation

Efforts to increase plant automation should be adopted in order to reduce labour costs and maximize security.

6.3.9. Selection of Activation method

There are three activation methods that can be adopted: namely physical-steam activation, CO_2/steam activation and KOH-chemical activation. The last, is less proven for tyres and does not differ substantially from physical activation. During steam activation though, the end product acquires satisfactorily qualitative, surface and structural, characteristics.

6.3.10. Energy balance

Aiming to improve the energy balance of activation, several energy conservation techniques are proposed. Pyrolysis oil (or part of it) can be used as fuel, either for the heating of the activation kiln and/or for the production of steam for physical activation. Electricity can also be produced (mainly for kiln rotation), if the cogeneration scheme would be adopted in order to produce simultaneously, electricity for the kiln rotation and steam for the activation chamber. Any excess electricity can be, possibly sold to the local power company. Heat recovery from high temperature flue gas can be also achieved [38].

7. Conclusions

The valorization of low-cost (even free of charge) waste materials has attracted special interest during the last decades. End of Life tyres can be initially pyrolysed and then activated, towards activated carbon production by physical (steam/CO_2) or chemical (potassium hydroxide) route. However, steam (physical) activation in a rotary kiln reactor at temperatures between 800 °C and 850 °C for a residence time which exceeds 2 h, is the proposed process from this study, based on sustainability criteria and end product characteristics.

This review study showed that the result of ELTs char activation is an activated carbon with medium adsorption capacity ($400–700 \, m^2 \, g^{-1}$) suitable for liquid and gas phase entrapment of organic substances, able to substitute coal or biomass based commercial products. The variety of possible uses, with the majority of them towards environmental depollution applications, can guarantee the commercialization of the end product.

A dual hybrid pyrolysis-activation technology can be viable, provided that markets for end products exist or, that they can easily be created and in parallel, if the whole plant is energetically self-sufficient. Based on experimental findings, the produced activated carbons using ELTs as raw materials, were found eligible for gas/liquid environmental depollution applications. Moreover, the use of pyrolytic gas to maintain the pyrolysis operational temperatures and of pyro-oil, both for the activation kiln and the cogeneration unit, along with the adoption of energy conservation technologies, can further improve the energy balance of the plant. With these techniques the pyrolysis-activation process, either operated in one or two kilns, offers the advantages of a positive operating cost with incomes originated from electricity exports.

A number of recommendations were made for a hybrid pyrolysis-activation technology development. These recommendations may enhance the creation of integrated solutions for ELTs management, aiming to their wider applicability through Europe.

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